

AKÜ FEMÜBİD 18 (2018) 011102 (62-66)

AKU J. Sci. Eng. 18 (2018) 011102 (62-66)

DOI: 10.5578/fmbd.66458

## Neodyum Katkısının FeBO<sub>3</sub> Oksit Malzemesinin Kristal ve Elektronik Özelliklerine Etkisi

Osman Murat Özkendir

Mersin Üniversitesi, Tarsus Teknoloji Fakültesi, Enerji Sistemleri Mühendisliği, Tarsus Kampüsü, 33400, Tarsus/Mersin  
e-posta: ozkendir@gmail.com

Geliş Tarihi:19.01.2017

; Kabul Tarihi:14.02.2018

### Özet

#### Anahtar kelimeler

Elektronik Yapı; Kristal Yapı; Nadir Toprak Metalleri; Soğurma Spektroskopisi

FeBO<sub>3</sub> oksit bileşiğine neodyum katkısının elektronik ve kristal yapısı üzerine etkileri Nd<sub>x</sub>Fe<sub>1-x</sub>BO<sub>3</sub> genel seri formülü ile çalışılmıştır. Ağır fermiyon seryum atomlarının örnekler içine katılanmasıyla polikristal yapıların ortaya çıktığı görülmüştür. Bu duruma, bor merkezli BO<sub>3</sub> ligand yapılarına metal Fe ve Nd atomlarının bağlanması sonucu ortaya çıktığı belirlenmiştir. Artan Nd katkısının, Fe düzlemlerinde bozulmaya neden olduğu, bununda polikristal yapıyı tetiklediği tespit edilmiştir. Kristal yapıların bünyesinde gerçekleşen elektronik etkileşme mekanizmalarını araştırmak üzere x-ışını soğurma ince yapısı tekniği (XAFS), x-ışını kırınım desenleri (XRD) ile koordineli olarak kullanılmıştır. Analizlerin sonucunda neodyum atomlarının f-seviyelerinin demir atomlarıyla olan zayıf etkileşmelerden sorumlu olduğu, bu nedenle güçlü elektron etkileşmelerinde en önemli etkileşme sahası olduğu tespit edilmiştir.

## Influence of Neodymium Doping on the Crystal and Electronic Properties of FeBO<sub>3</sub> Oxide Materials

### Abstract

#### Keywords

Electronic Structure; Crystal Structure; Rare Earth Metals; Absorption Spectroscopy

Neodymium substitution in titanium coordinations of the FeBO<sub>3</sub> materials were studied with their crystallographic and its related electronic structure properties according to the general formula Nd<sub>x</sub>Fe<sub>1-x</sub>BO<sub>3</sub>. With the doping of the heavy fermion "Neodymium", samples were formed in polycrystalline structure due to boron centered ligands BO<sub>3</sub>. With the increasing Nd in the samples, disturbances on the Fe planes became more clear and it supports geometrically different crystal structures formations. Electronic structure properties were investigated by the X-ray Absorption Fine Structure Spectroscopy (XAFS) technique both to obtain the electronic mechanisms in the crystals and to support crystal structure study of the samples carried with the X-ray diffraction (XRD) patterns. As a result of the analysis, f-levels of the Neodymium atoms were determined not as the main playground of interplays and 5d-3d mixing were determined to emerge dominant interactions causing phase transitions.

© Afyon Kocatepe Üniversitesi

### 1. Introduction

Technological interest in every field of life cause a huge demand in scientific investigations materials to improve their properties, such as electrical, optical, crystal, magnetic, electronic etc. [Ruihua et al. 2001; Nabi and Pentcheva 2011; Lufoso and Woodward 2001]. Especially, with the discovery of the unusual

properties (crystal, optical, electrical, magnetic and electronic) of Rare-Earth orthoborates (REO) made them as an important material for researches. Most of studies on materials containing 3d row Transition Metals (TM) and 4f row Rare-Earths (RE) materials revealed interesting interplays between 3d and 4f electrons and this phenomena attracted scientists' attentions due to desired characteristics for

technological applications. Transition metals (TM) and their oxides are known from the ancient times and due to their abundance in the earth's crust, they became indispensable materials in technological applications with preferred magnetic, electronic, chemical or crystallographic properties [Ruihua et al. 2001; Nabi and Pentcheva 2011; Lufoso and Woodward 2001]. 3d metals owe their popularity to their d shells which are partly occupied and cause strong correlations with the neighboring atoms' electrons and emerge huge number of interesting physical phenomena with desired technological outcomes. Neodymium (Nd) doped  $\text{FeBO}_3$  structure were studied to probe the influence of 4f electrons on the electronic structure of the  $\text{FeBO}_3$  oxide and the response of crystal structure to the substitution mechanism. Sample series of  $(\text{Nd}_x\text{Fe}_{1-x})\text{BO}_3$  material was studied. In the study, boron atoms were treated as the key agent due to its high affinity.

$\text{FeBO}_3$  (Ferric Borate) is an intensively studied member of this group as a weak antiferromagnetic material at Néel Temperature of  $T_N = 350$  K and it is the reference material of this study [Liu et al. 2005].  $\text{FeBO}_3$  has strong electron correlations among its atomic environment showing interesting magneto-optical properties and provides spontaneous magnetization at room temperature via combining optical transparency in the visible region.

In this study, new, Rare-Earth Metal doped ferric borate compound structures were investigated both for crystal and electronic structures. Because of the interesting properties of narrow 4f levels, the rare earth element Nd kept in the heart of the structure [Bernal et al. 1963]. Valence fluctuations are the most exciting behaviors of f-electron systems that play an essential role in phenomena, such as unconventional superconductivity.

## 2. Materials and Method

Samples were prepared at MEITAM laboratories of Mersin University (Mersin, Turkey). Rare-Earth Oxiborate samples, with general formula  $(\text{Nd}_x\text{Fe}_{1-x})\text{BO}_3$ , were synthesized from the stoichiometric

mixtures of  $\text{Nd}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$  (hematite) and  $\text{B}_2\text{O}_3$  powder compounds with high purity (>99.99%). To obtain the sample powders, stoichiometric amounts were mixed and milled for 30 minutes and annealed in the furnace at  $550^\circ\text{C}$  for 4 hours. After first annealing, powders were milled again for 30 minutes and annealed in the furnace at  $950^\circ\text{C}$  for 48 hours. XRD patterns were taken to study the crystal properties of the samples at the MEITAM laboratories with Rigaku Smartlab. Accordingly, electrical resistivity of the samples were also measured with the four probe technique at room temperatures (RT). Advanced crystal structure analysis on the crystal structure were performed by the MAUD software [Lutterotti et al. 2004].

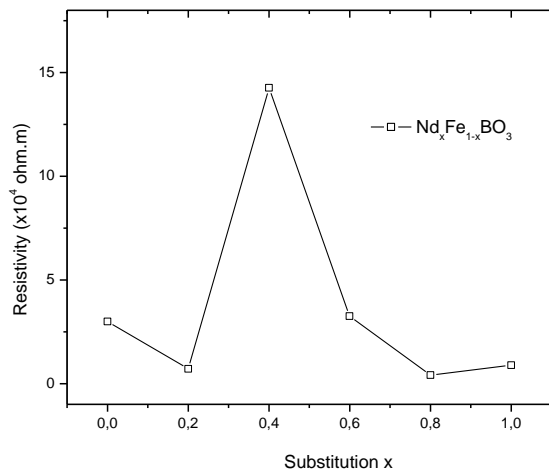
To support the vague details appeared during the crystal structure analysis, XAFS (X-ray Absorption Fine Structure) measurements were performed at Beamline-BL8:XAS of SIAM Photon facility (SLRI) (Nakhon Ratschaisima, Thailand) for Fe K-edge of the  $(\text{Nd}_x\text{Fe}_{1-x})\text{BO}_3$  samples at room temperature [Klyusubun et al. 2006; Klyusubun et al. 2007]. XAFS measurements can provide so special and high resolution data which can illuminate both the electronic and crystal structure of the interested materials.

Additionally, magnetic properties of Nd substituted ferric borate samples were tested with PPMS system with Field Cooled measurements under 1kOe magnetic field and substituted samples were determined to have paramagnetic ordering at the room temperatures. Sample has paramagnetic ordering until 50 K, however below this temperature an uncompleted magnetic phase transition ( $\sim 5\text{K}$ ) was observed to ferromagnetic ordering.

## 3. Results and Discussion

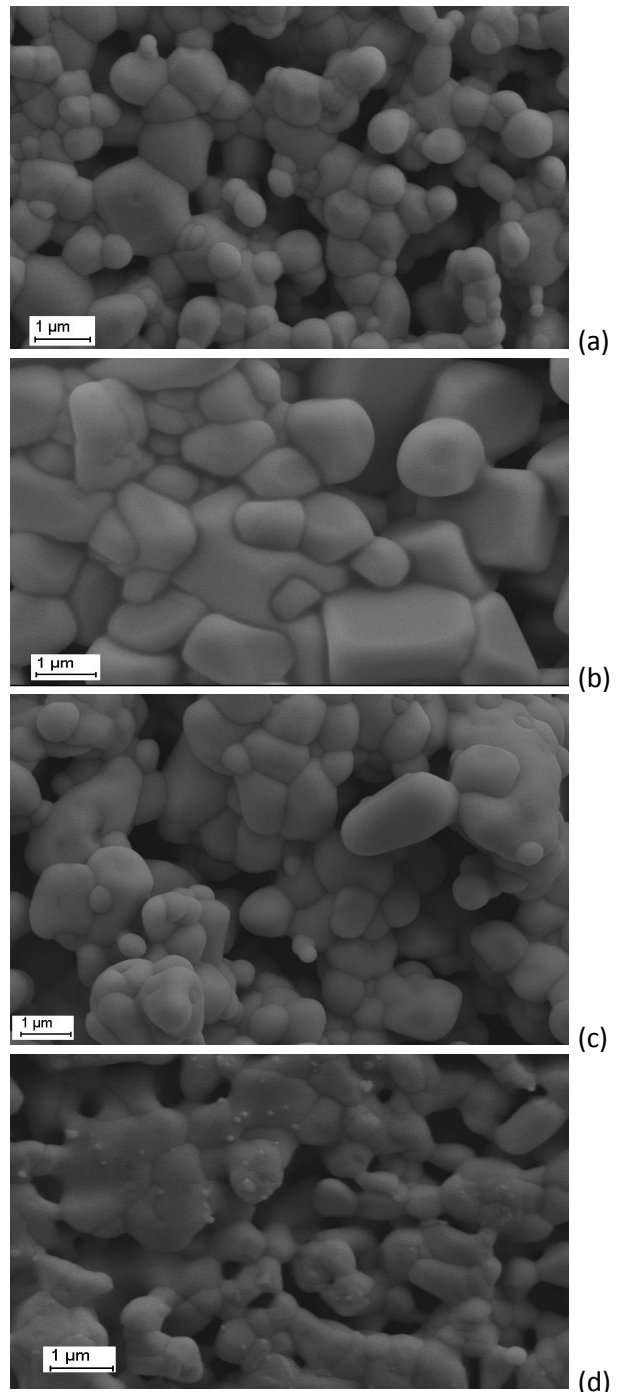
Electrical properties of Nd substituted  $\text{FeBO}_3$  samples were tested with the four probe technique and resistivity results of the samples are given in Figure 1. The results of the measurements were determined in the category of semiconductors varying between  $0.11 \sim 38.0 \cdot 10^4$  ohm.m. The

response of the electrical resistivity to the Nd substitution process reveals a decrease for 20% substituted sample followed by a sharp increase for 40% substituted sample followed by a sharp increase for 40% substituted sample highlighting a crystal anomaly that provide worse conductivity results.



**Figure 1.** Results of electrical properties of Nd substituted FeBO<sub>3</sub> samples which were tested with the four probe technique.

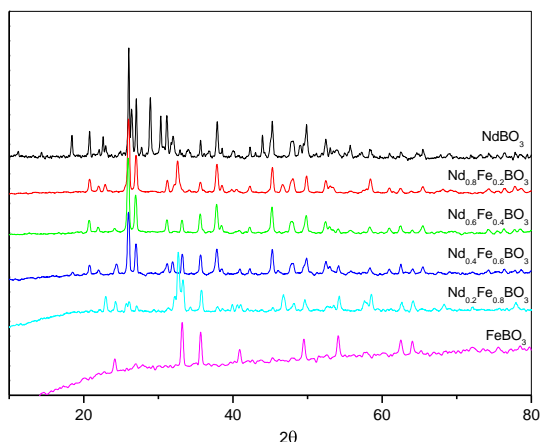
Nd doping revealed a disturbance in the FeBO<sub>3</sub> that yields better electrical conductivity at room temperatures due to more porous structure via large Nd atoms, excluding the sample for x=0.4. Electrical properties of the materials are highly related with the crystal morphology and structural properties of the samples [Salah et al. 2009]. It was reported in several studies that porous materials provide more distances to electrons to hop and give rise to the conductivity of the material. In figure 2 (a, b, c, d), SEM images of the Nd-substituted samples are given. According to the images, substituted samples (except for x=0.4 substituted) have high agreement both in surface morphology and porosity. However, for the sample with 40% Nd-substitution, no porosity observed on the surface. This image also confirms the relation between porosity and conductivity. The granular structure with high porosity for materials are widely used in modern electronics which provides interactions of regions easily via electron transfers.



**Figure 2.** SEM images of the Nd-substituted samples (a) x=0.2 (b) x=0.4 (c) x=0.6 (d) x=0.8

Crystal structure properties and its related morphology can be studied best by the XRD patterns. XRD patterns of the samples are given in comparison in figure 3. According to the analysis results of XRD patterns; excluding the parent oxide FeBO<sub>3</sub>, all patterns show noisy patterns reflecting polycrystalline nature of the samples. The parent oxide sample ( x=0.0) has less reflection peaks and was determined to have one type of crystal

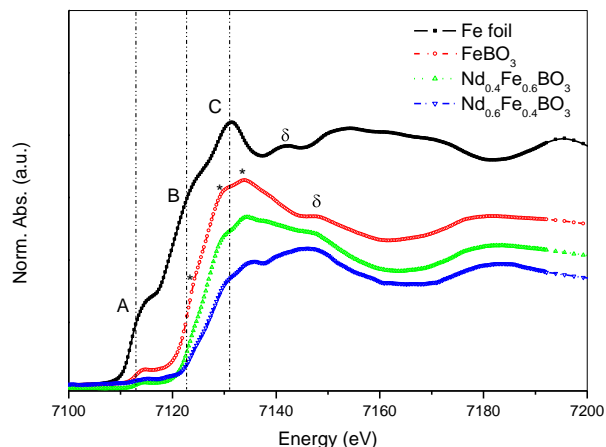
structure in the bulk with trigonal rhombohedral geometry and “R-3c:H” space group symmetry, i.e., FeBO<sub>3</sub>.



**Figure 3.** XRD patterns of the samples.

The reflection peaks for the FeBO<sub>3</sub> crystal appeared in other substituted samples but with a decay parallel to the substitution amount. Determined lattice parameters are: a=b= 5.306 Å and c=13.751 Å. Second parent oxide sample for x=1.0 (NdBO<sub>3</sub>) was determined as formed in orthorhombic geometry with space group of “Pnma”. The lattice parameters for the sample were determined as: a=b= 5.740 Å and c=8.080 Å. The XRD patterns of the substituted samples have reflection peaks of both parent oxides as a combination of two crystal structure formed in the bulk: trigonal and orthorhombic. So the sample show the properties of both parents partly.

Background information beneath the atomic tendencies to form separate crystal structures by the substituted neodymium and iron can best analyzed with an electronic structure study. Electronic structure properties were studied by XAFS technique via data collection from the Fe K-edge from the iron atoms in the Nd-substituted samples. The XAFS study should be divided in three parts; pre-edge, main-edge and post-edge.



**Figure 4.** Comparison of the XANES spectra of Nd<sub>x</sub>Fe<sub>1-x</sub>BO<sub>3</sub> samples

Comparison of the XANES spectra of Nd<sub>x</sub>Fe<sub>1-x</sub>BO<sub>3</sub> samples are given for Fe-foil, FeBO<sub>3</sub> and Nd-substituted samples (x=0.4 and 0.6) in figure 4. To avoid the complexity during analysis, only 40% and 60% neodymium substituted samples are given as small steps around equilibrium. Iron K-edge XAS spectra of the samples begin to rise at 7104 eV and give maxima (assigned as “C”) at 7132 eV for the Fe-foil. Due to molecular interactions, oxidation states changed in all samples, excluding the Fe-foil, and new ionic state cause a slight shift on the edge energy positions. The main absorption edge energies for the parent oxide FeBO<sub>3</sub> and Nd-substituted samples for x=0.4 and 0.6 are 7129.6 eV, 7128.8 eV and 7129.3 eV, respectively. Main absorption peaks (“B” and “C”) are due to the 1s electrons’ transitions to the unoccupied 4p levels. According to the quantum selection rules 1s electrons’ transition to 3d unoccupied levels as a final state is forbidden. The only way for 1s electrons to make transitions to d-level is p-symmetry existence on the molecular band via hybridization or mixing. If such an overlapping occurs, a peak below the main edges appear as an indicator of forbidden transitions and called “pre-edge” region. On the K-edge spectra of all samples a tiny pre-edge feature appeared and assigned as “A”. Low intensity of the pre-edge feature highlights the weak mixing between 4p levels and 3d level of Fe. Beyond the pre-edge structure, the main edge spectra have

three weak slopes that corresponds to the  $p_{x,y,z}$  on the 4p molecular bands which are assigned with “\*”. The pre-edge and the main edge of the substituted samples proves the “no interaction” between 3d levels of iron and 4f levels of neodymium occurred. However, these two atoms interact weakly with each other via the overlapped 3d-5d levels and built up metal bonding that appeared as post edge beyond the main edge assigned as “ $\delta$ ”.

#### 4. Conclusions

In this study, materials with the general formula  $Nd_xFe_{1-x}BO_3$  were investigated upon their crystal, electrical and electronic properties. Among the substituted samples, sample for  $x=0.4$  was determined the most interesting sample showing worst conductivity with non porous crystal structure. Besides, the relation between grain size and resistivity was also confirmed. Low pre-edge intensity below the iron K-edge spectra of the samples confirmed the weak mixing between 4p levels and 3d level of Fe. No f-level interaction between TM Fe and RE Nd was observed but weak Fe 3d and Nd 5d mixing observed with a post edge peak on the spectra. Due to weak atomic interactions, both iron and neodymium were determined as tending to form different crystal structure with different geometries by linking to  $BO_3$  ligands.

#### Acknowledgement

The author would like to thank to Dr. Gunnar Ohrwall from MAX-lab. Beamline I1011 (Lund, Sweden), to Dr. Wantana Klysubun and her staff from SLRI (Siam Photon) both for their technical support and great hospitality. This study is supported financially by “BAP-TTEF EEEME (OMO) 2012-7” project of Mersin University

(Mersin, Turkiye). Additionally, the research leading to these results has received funding from the European Community's Seventh Framework Program (FP7/2007-2013) CALIPSO under grant agreement no 312284.

#### References

- Bernal I., Struck C. W., White J. G., (1963), New transition metal borates with the calcite structure, *Acta Crystollography* 16, 849
- Klysubun W., (2007), *Nuclear Instruments and Methods in Physics Research A* 582, 87W.
- Klysubun W., (2006), X-ray Absorption Spectroscopy Beamline at the Siam Photon Laboratory, *AIP Conference Proceedings* 879, 860
- Liu Y.W., Rui X.F., Fu Y.Y., Han Zhang Y.W, (2005), Synthesis of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> Nanowires and its Magnetic Properties, *Journal of Metastable and Nanocrystalline Materials* 23, 243
- Lufoso M.W., Woodward P.M., Prediction of the crystal structures of perovskites using the software program SPUDS, (2001), *Acta Crystollography B* 57, 725-738
- Lutterotti L., Chateigner D., Ferrari S. and Ricote J., (2004), Texture, residual stress and structural analysis of thin films using a combined X-ray analysis, *Thin Solid Films*, 450 34-41
- Nabi H. S. and Pentcheva R., Energetic stability and magnetic coupling in (Cr 1- x Fe x) 2 O 3: Evidence for a ferrimagnetic ilmenite-type superlattice from first principles, (2011), *Physical Review B* 83: 214424
- Ruihua C., Borca C. N., Dowbena P. A., Stadler S., Idzerda Y. U., (2001), Potential phase control of chromium oxide thin films prepared by laser-initiated organometallic chemical vapor deposition, *Applied Physics Letters* 78(4), 521-528
- Salah A. Makhlof, Mohamed A. Kassem, M. A. Abdel-RahimMakhlof, (2009), Particle size-dependent electrical properties of nanocrystalline NiO, *Journal of Materials Science* 44:3438–3444